

# The Stability of Cellulose: A Perspective from the Statistical Mechanics of Hydrogen Bond Networks

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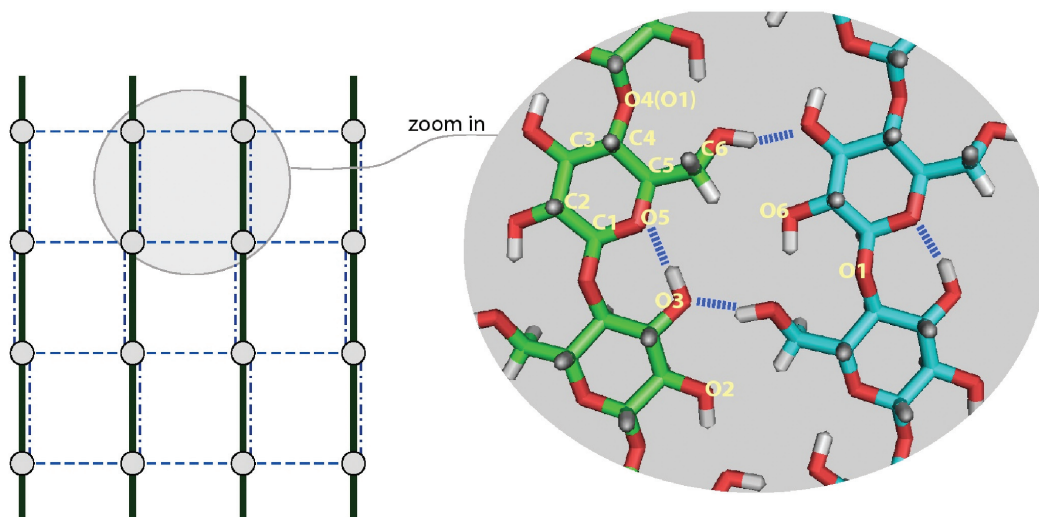
*Fig. 1. An illustration of the sheet structure of cellulose I- $\beta$ . Cellulose chains (solid vertical rods) are linear collections of monomers (filled circles), which can be potentially linked using H-bonds residing in intrachain (vertical, dot-dashed lines) and interchain positions (horizontal, dashed lines).*

Biofuels derived from lignocellulosic biomass offer a cleaner and sustainable alternative to fossil fuels, with several advantages over ethanol derived from corn and sugarcane. Challenges encountered during the conversion of biomass to ethanol are critically linked to the uncertainties of the physical properties of the feedstock. In particular, a better understanding of cellulose and its biodegradation will allow one to address the factors preventing an efficient fuel economy based on cellulosic biomass conversion. A central problem is how cellulose, an assembly of polymers of glucose, can be effectively isolated and disassembled to its basic building block, glucose. The underlying stability of cellulose comes from the dense hydrogen bonding (H-bond) network constructed among the crystalline-ordered polysaccharide chains. We have performed computations both at the atomistic and coarse-grained level to investigate the thermal responses of various H-bonding networks of cellulose. Here

we describe the results from coarse-grained computations of H-bonding in cellulose I- $\beta$ , the main form of cellulose found in plants.

We constructed a statistical mechanical model at the resolution of explicit H-bonds that takes into account both intrachain and interchain H-bonds in naturally occurring cellulose crystals. As shown in Fig.1, the stability of a sheet of chains in I- $\beta$  is considered using a statistical description of H-bonding networks on a square lattice. The partition function and subsequent statistical properties of this lattice were calculated using the transfer matrix method. This theoretical model describes the state of the system as a collection of discrete representations of the state of each potential H-bonding position, i.e., each type of H-bond is either formed or not formed at a position. In such a binary description, when a bond is formed we associate it with a gain in bonding energy. Similarly, a gain in entropy is assigned when H-bonds are absent for a particular bonding position. The specific gain in entropy also depends on its neighboring states. Finally, we can associate each particular state of the hydrogen bond network with a statistical weight based on its free energy. A major simplification that makes the evaluation of the partition function of this lattice model solvable is that consideration is limited to “native” H-bonds.

Our calculations suggest that such plasticity of an H-bonding network (owing to frustration and seeming redundancy of the H-bonding elements) keeps the overall H-bonding stability persistent over a wide range of temperatures. An interesting and unique feature of this assembly is the multiple possibilities of H-bonding patterns within a single, stable structure of the cellulose. Instead of only one stable pattern, different H-bonding patterns dominate at different temperatures until the disassembly occurs at very high temperatures. As shown in Fig. 2., intrachain H-bonding is more stable than the interchain bonding throughout the temperature range that is considered. This model is able to capture important equilibrium properties at the resolution of individual bonds (see Fig. 3). Specifically, we found that intrachain H-bond O3 H3  $\cdots$  O5 is always stable until disassembly. Intrachain H-bond O2 H2  $\cdots$  O6, and



interchain H-bonds  $O6-H6 \cdots O3$  and  $O6-H6 \cdots O2$ , are stable at low temperature. However, with increasing temperature, the H-bonding network undergoes a switch in the connectivity of H-bonds. A role exchange between donor and receptor for the two hydroxyl groups  $O6-H6$  and  $O2-H2$  is observed. As a result, H-bond  $O2-H2 \cdots O6$  switches off as an intrachain H-bond and shows up as an interchain H-bond. These computations may provide useful clues on rational design for the efficient degradation of cellulose.

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#### References

T. Shen, S. Gnanakaran, *Biophys.J.*, April issue vol. 96, in press (2009).

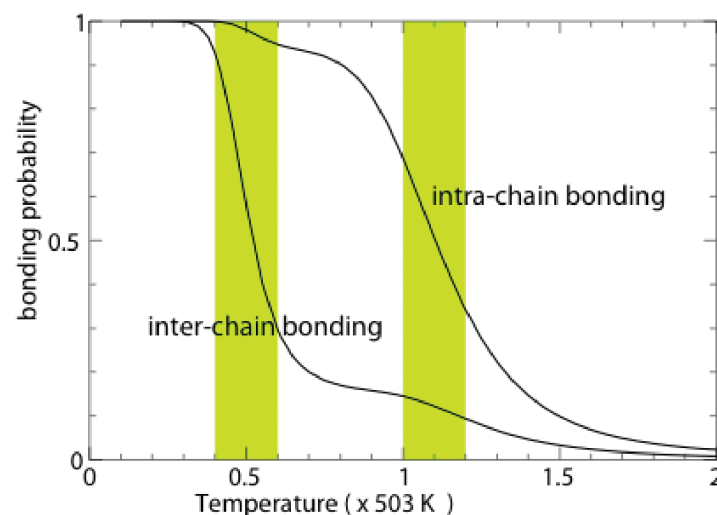


Fig. 2. The intrachain and interchain H-bonding probabilities are shown as a function of temperature.

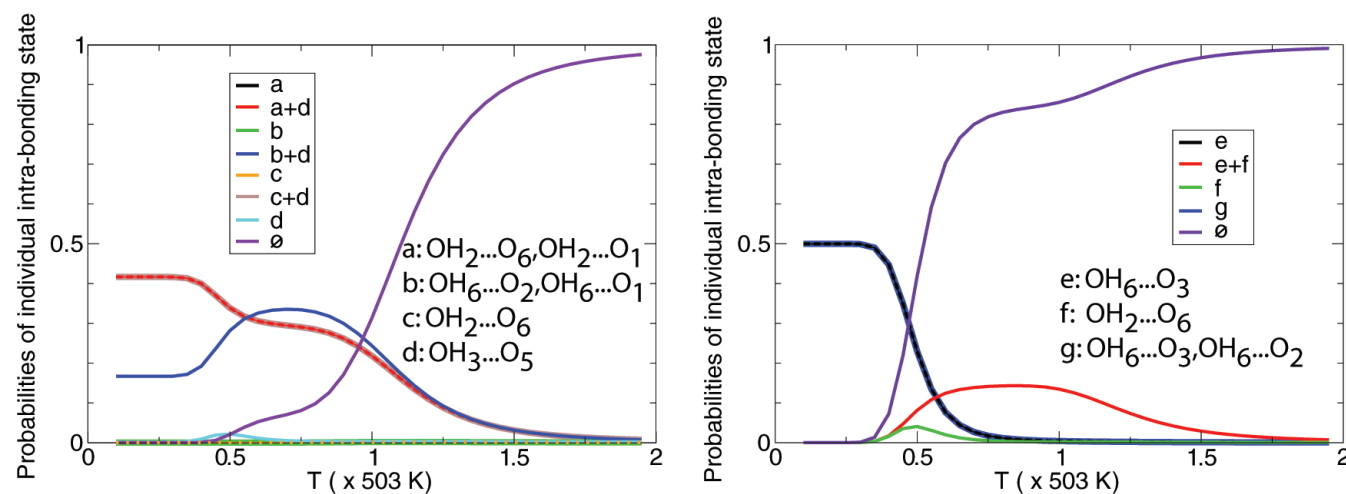


Fig. 3. The probabilities of individual states (different colors) of intrachain H-bonding (left) and interchain H-bonding (right) are shown as a function of temperature.

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